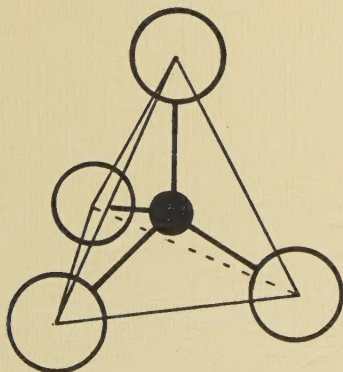


SILICATES IN THE SOLID STATE

A Structural Study of Some Silicate Ions

Håkan Annehed



Lund 1985

Annehed, H. (1985)

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Chemical Center, University of Lund

P.O. Box 124, S-221 00 Lund, Sweden

To my children

Sara Jacob Stina

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Abstract The crystal structure of $\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2$, $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cs}_{0.35}\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6$, janhaugite and kvanefjeldite have been studied. All structures were determined with X-ray diffraction techniques. The structure of the investigated compounds are described. They are built up in different ways, containing isolated SiO_4^{4-}-tetrahedra, isolated $\text{Si}_2\text{O}_7^{6-}$-groups, layer or framework silicates. Factors related to the Si-O bond length variation, such as the sum of bond strengths and the mean coordination of the oxygen atoms, the influence of the non-tetrahedral cations, the Si-O-Si and O-Si-O angles are discussed.			
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H. Annehed, Inorganic Chemistry 2, Chemical Center, P.O.Box 124, S-221 00 Lund, SWEDEN

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Date 1985-04-10

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I INTRODUCTION

The synthesis and structure determination of silicates are parts of a research programme at this institute. This review summarizes structural studies on five silicates. Two of these are minerals. All structures were determined using single-crystal X-ray techniques. The aim of the single-crystal investigations was to determine the bond lengths and the geometrical arrangement of the silicate ions and the coordination polyhedra about the cations. The results have been reported in the following papers.

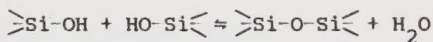
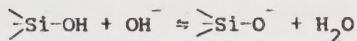
1. The crystal structure of $\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2$.
Fälth, L. and Annehed, H. (1984) Z. Kristallogr. (in press).
2. The crystal structure of janhaugite, a sorosilicate of the cuspidine family.
Annehed, H., Fälth, L. and Raade, G. (1985) N. Jb. Miner. Mh., H.1, 7-18.
3. Crystal structure of kvanefjeldite: The introduction of $\infty[\text{Si}_3\text{O}_7\text{OH}]$ layers with eight-membered rings.
Johnsen, O., Leonardsen, E.S., Fälth, L. and Annehed, H. (1983) N. Jb. Miner. Mh., H.11. 505-512.
4. Crystal structure of synthetic makatite $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.
Annehed, H., Fälth, L. and Lincoln, F.J. (1982) Z. Kristallogr., 159, 203-210.
5. The crystal structure of $\text{Cs}_{0.35}\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6$, a cesium-aluminosilicate with the blakitaite framework.
Annehed, H. and Fälth, L. (1984) Z. Kristallogr., 166, 301-306.

The form of the silicate ions, in the compounds which have been studied, are quite different. The structures are built up of isolated SiO_4^{4-} -tetrahedra, isolated $\text{Si}_2\text{O}_7^{6-}$ -groups, layer- or framework silicates. Experimental details are given in chapter II and a short description of the structures is given in chapter III. Some factors influencing the Si-O distances are discussed in chapter IV.

Silicate structures

From the electronic configuration of silicon in the ground state, $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^0 3d^0$, it follows that the silicon atoms generally form bonds to four oxygen atoms, in a tetrahedral sp^3 hybrid. The silicon-oxygen distances are about 1.6 Å. This SiO_4^{4-} -tetrahedron is the primary building unit. In many silicate structures the silicon atoms are replaced by aluminium atoms in the tetrahedra centre.

In solution, silica exists as the monomer, $Si(OH)_4$, or in high pH, as silicate ions (Alexander et al., 1954). Depending on concentration and pH a complicated series of polymerisation-depolymerisation equilibria of the type shown below takes place. This leads to the formation of different species (Dent Glasser and Lachowski, 1980).



The species formed, and the size and charge of the hydrated cations, control the nucleation process. The possibility of linking two or more tetrahedra together by sharing an oxygen atom (corner-sharing of tetrahedra) leads to the formation of a great number of different silicate ions.

A SiO_4^{4-} -tetrahedron is called singular, primary, secondary, tertiary and quaternary when it shares zero, one, two, three or four corners respectively. Bragg (1930) classified the silicate structures based on linkage of corner-shared SiO_4^{4-} -tetrahedra. This classification is still actual today, but has been refined by Zoltai (1960) and Liebau (1962, 1972, 1978). Zoltai added two criteria to the customary silicate classification: the size of the tetrahedral groups and a numerical expression called the sharing coefficient based on the different nature of the corner-sharing of tetrahedra. The classification made by Liebau is based on linear condensation of SiO_4^{4-} -tetrahedra.

A short review of different silicon-oxygen complexes and a few examples of compounds are given in the following paragraphs. Two kinds of models are used to illustrate silicate structures. These are:

1. Polyhedra such as the tetrahedron and octahedron, used to represent the SiO_4^{4-} and MO_6 -groupings (Fig. 1a).
2. Connected frameworks of silicon atoms alone (Fig. 1b).

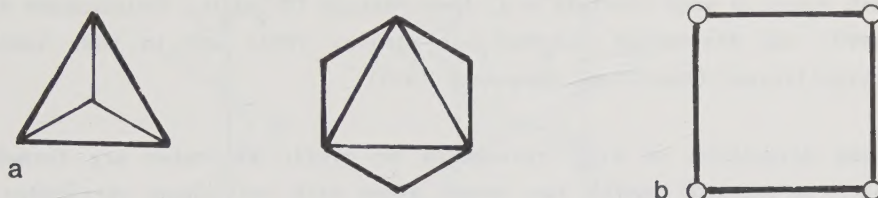


Fig. 1. (a) tetrahedron and octahedron (b) linkage of four SiO_4^{4-} -tetrahedra

The main types of silicate structures are summarized below according to the form of the silicate ions created by the linkage of SiO_4^{4-} -tetrahedra, as in the conventional classification.

Nesosilicate	isolated SiO_4^{4-} -tetrahedra
Sorosilicate	isolated groups of SiO_4^{4-} -tetrahedra
Inosilicate	chain silicate
Phyllosilicate	layer silicate
Tektosilicate	framework silicate

Neso-silicates

This group contains structures with isolated SiO_4^{4-} -tetrahedra, and the SiO_4^{4-} -ion is named the orthosilicate ion. The cations are coordinated to a number of oxygen atoms in the SiO_4^{4-} -ions, depending on their size. Phenacite (Be_2SiO_4 ; Zachariasen, 1971), olivine ($(\text{Mg,Fe})\text{SiO}_4$; Birle et al., 1968), zircon (ZrSiO_4 ; Robinson et al. 1971) and garnet ($\text{M}_2^{\text{III}} \text{M}_3^{\text{II}} (\text{SiO}_4)_3$ where $\text{M}^{\text{II}} = \text{Ca, Mg, Fe, Mn}$ and $\text{M}^{\text{III}} = \text{Al, Fe, Cr}$; Novak and Gibbs, 1971) are important structure types of this group. The formation of isolated $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$ and $\text{SiO}_3(\text{OH})^{3-}$ ions are known from hydrated silicates of the alkali- and alkali-earth metals (Schmid et al., 1979; Dent Glasser and Jamieson, 1976; Malik and Jeffery, 1976).

Soro-silicates

Condensation of two SiO_4^{4-} -tetrahedra forms a $\text{Si}_2\text{O}_7^{6-}$ -group or the pyrosilicate ion (Fig. 2a). The angle between the two silicon atoms and the bridging oxygen can vary widely, from 125° to 180° (Baur, 1971). The $\text{Si}_2\text{O}_7^{6-}$ ions are found in some minerals e.g. thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$; Cruickshank et al., 1962) and åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$; Kimata, 1983) and in some lanthanoid pyrosilicates (Smolin and Shepelev, 1970).

Ring structures of SiO_4^{4-} -tetrahedra or cyclic silicates are formed when each tetrahedron shares two oxygen atoms with contiguous tetrahedra (Fig. 2b). The silicate ions have the formula $[\text{SiO}_3^{2-}]_n$ where $n = 3, 4, 6, 8, 9, 12$. The most common are $n = 3$ and 6. They exist in benitoite ($\text{BaTiSi}_3\text{O}_9$; Fischer, 1969) and beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; Gibbs et al., 1968).

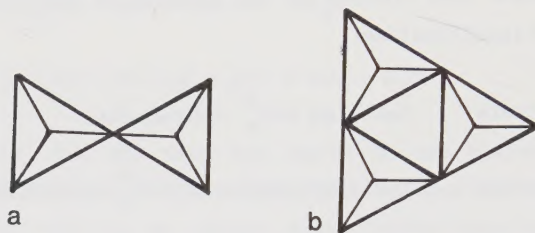


Fig. 2. Examples of isolated SiO_4 -groups (a) $\text{Si}_2\text{O}_7^{6-}$ (b) $\text{Si}_3\text{O}_9^{6-}$

Ino-silicates

Structures with corner-sharing SiO_4^{4-} -tetrahedra forming single chains silicate ions, $[\text{SiO}_3^{2-}]_n$, are very common in many minerals e.g. the pyroxenes (Fig. 3a). The single chains may be classified according to periodicity of tetrahedral groups in the chain structure. Silicate chains with repeat units containing 2, 3, 4, 5, 6, 7, 9 and 12 tetrahedra are known (Liebau, 1972).

Double chains are built up from two corner-sharing single chains. The amphiboles, which form a large silicate group, consist of two pyroxene chains. The composition of these double chains depends on the number of tetrahedra taking part in the connection (Fig. 3b).

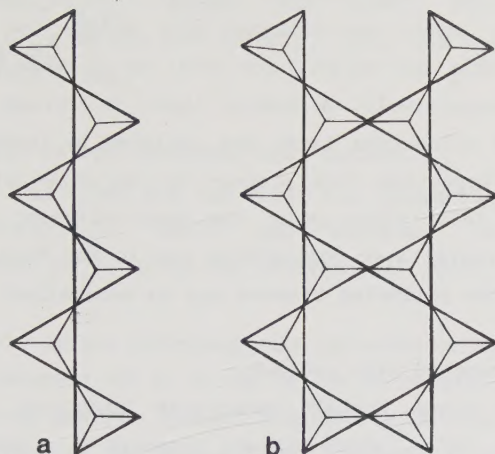


Fig. 3. Examples of single chain and double chain found in (a) the pyroxenes and (b) the amphiboles

Phyllosilicates

Linkage of single chains or single rings will result in continuous single layers with the empiric formula $[\text{Si}_2\text{O}_5^{2-}]_n$. Layers built up of rings containing 6 tetrahedra or 4 and 8 tetrahedra are the most common, but layers with 4, 6 and 8 rings or 4, 6 and 12 rings are known (Fig. 4).

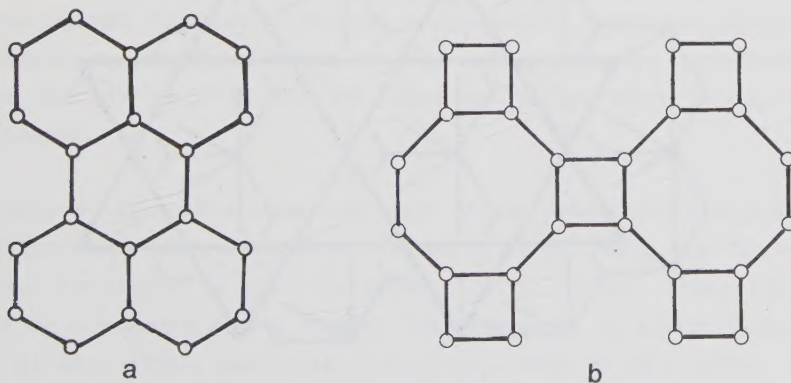


Fig. 4. Schematic representation of the structures of layer silicate containing rings of (a) 6 tetrahedra and (b) 4 and 8 tetrahedra

If the unshared oxygens are on the same side of a layer, two layers form a double layer by sharing these oxygen. Another type of layer is generated when single silicate layers are combined with $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ layers. The structure of $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ are built up of edge-sharing Al and Mg octahedral layers respectively. A double layer is formed when OH groups from one side of the octahedral layer are replaced by unshared oxygen from the silicate layer. Repeating this process on the other side of the octahedral layer results in a triple layer. The many different types of layered silicates differ in their layer composition and in the filling of the space between the layers. The following classes can be recognized:

a. Single layers connected with cations.

Members of this class include sanbornite (Douglass, 1958) and apophyllite (Prince, 1971), which contain rings of 6, 4 and 8 SiO_4^{4-} -tetrahedra respectively in the layers.

b. Double layers connected with cations.

This type of layer exists in e.g. $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$ (Takéuchi and Donnay, 1959) and $\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$ (Takéuchi, 1958), where some silicon are replaced by aluminium. Otherwise the layer would be neutral.

c. Uncharged double layers.

The empiric formula of the layers are $\text{Mg}_3(\text{OH})_4\text{Si}_2\text{O}_5$ or $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$ and they exist in chrysotile (Whittaker, 1956) and kaolinite (Zvyagin, 1960) (Fig. 5).

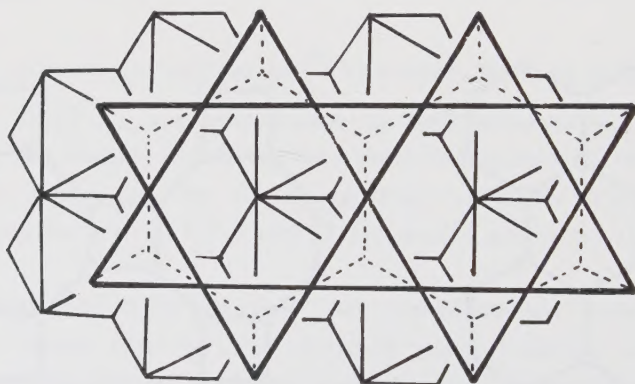


Fig. 5. One layer of SiO_4^{4-} -tetrahedra shares corner with one layer of aluminium octahedra found in kaolinite

d. Uncharged triple layer.

Talc ($\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$; Rayner and Brown, 1966) and pyrophyllite ($\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10}$; Wardle and Brindly, 1972) are well-known minerals belonging to this class.

e. Charged triple layers connected with cations.

Included in this class are the micas e.g. phlogopite ($\text{KMg}_3(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$; Hazen and Burnham, 1973) and muscovite ($\text{KAl}_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$; Birle and Tettendorst, 1968).

f. Charged triple layers connected with hydrated cations.

Partial replacement of Al by Mg in the octahedral sites will result in a layer having smaller charges per unit area than in e (above). Montmorillonite (Cowley and Goswami, 1961) belongs to this group.

g. Charged triple layers connected with another type of layer.

The chlorite minerals are included in this group. The three layers are connected by brucite layers ($\text{Mg}(\text{OH})_2$), where some Mg^{2+} are replaced by Al^{3+} resulting in a positively charged layer.

Tektosilicates

When all of the oxygen atoms in the SiO_4^{4-} -tetrahedra are shared by two tetrahedra a three-dimensional continuous framework structure are formed. This is found in the various forms of SiO_2 . Replacing Si^{4+} by Al^{3+} the framework will have the composition $[\text{Al}_x\text{Si}_{1-x}\text{O}_2^{x-}]_n$. In order to balance the negatively-charged framework, cations are present. These are situated in the channels or cavities formed by the aluminosilicate framework. The feldspars and the zeolites are two important groups which belong to the tektosilicates.

Fig. 6 shows a layer of a structural unit of the feldspars. This unit consists of $(\text{Al},\text{Si})\text{O}_4$ -tetrahedra forming 4 and 8 rings. where the fourth vertex in the tetrahedra is pointing either "up" or "down". These layer are connected by a symmetry plane, forming the framework. In albite ($\text{NaAlSi}_3\text{O}_8$; Ferguson et al., 1958), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$; Cole et al., 1951), orthoclase (KAlSi_3O_8 ; Colville and Ribbe, 1968) and celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$; Newnham and Megaw, 1960) the cations are placed in the cavities. The structural differences found in the feldspars depend on the Si/Al ratio in the framework and the size of the cations.

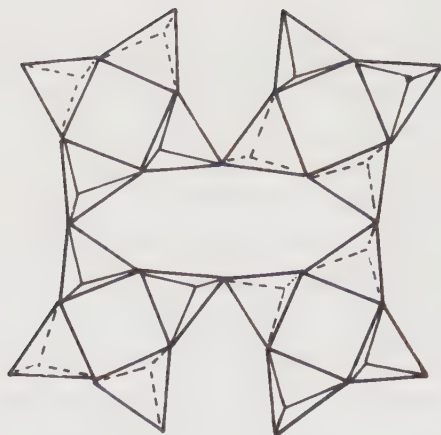


Fig. 6. Idealized drawing of the feldspar structure

All zeolites have a framework that encloses large open cavities or tunnels, containing the cations and water molecules. Over 40 zeolites with different frameworks are known. For an excellent review see Breck (1974). The zeolites have many important properties which have a structural interpretation e.g. cation exchange and catalytic properties and adsorption of gases and vapours. Fig. 7. shows a drawing of the framework found in bikitaite (Kocman et al., 1974).

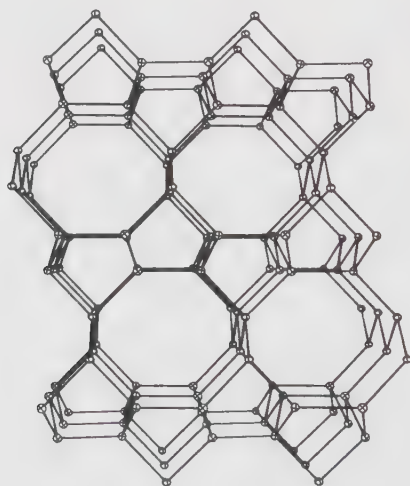


Fig. 7. The framework found in bikitaite

II EXPERIMENTAL

Denotations of the investigated compounds are given in Table 1.

Preparative work

Investigation of the silicon-rich part of the $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ system led to the preparation of a number of hydrous silicates: makatite (Sheppard et al., 1970), $\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ (McCulloch, 1952 and Iler, 1964), magadiite (Eugster, 1967 and McAtee et al., 1968) and kenyaite (Eugster, 1967) (see Fig. 8).

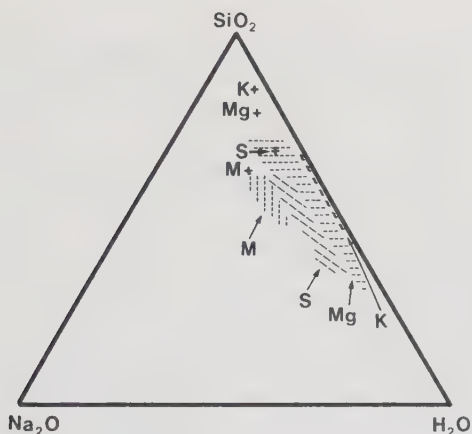


Fig. 8. Reactant composition diagram. Areas identified by letters refer to compositions which yield the hydrous silicates: M (makatite); S ($\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$); Mg (magadiite); K (kenyaite). The points marked with (+) show the composition of the phase. Compositions in weight percent.

The method consists of dissolving AR NaOH in water, cooling the solution to 20°C and then adding amorphous SiO_2 (containing $\sim 15\%$ H_2O). The mixture was carefully stirred and cooled, until the slurry hardened into an opaque gel, which was then transferred to stainless steel bombs. The bomb, which was sealed by screwing the lid into a copper ring gasket, was heated to temperatures between $120-150^\circ\text{C}$ for periods of 1-2 weeks. For makatite (IV), the product was a hard opaque solid in contact with residual solution, but for the other compounds a slurry resulted. As it was shown that water washing of the silicate product destroys the innercrystalline arrangement by removing Na^+ without altering the crystal shape, all crystal-

line products were leached from the gel with NaOH solution ($\text{pH} \approx 10-11$). The substitution of structural sodium ions by protons is indicated in Fig. 9, where the titration curve obtained when 0.50 g synthetic makatite (IV) is titrated with $0.100 \text{ mol l}^{-1} \text{ HCl}$ in 150 ml H_2O is shown.

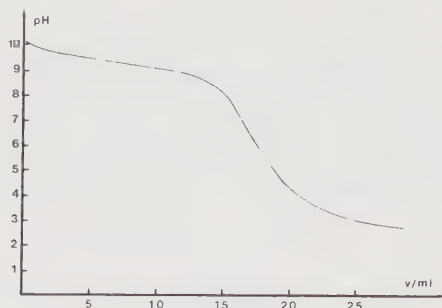


Fig. 9. Titration curve

(Extraction of Na^+ by repeated washings with water was also a problem in the preparations of kanemite, Beneke and Lagaly, 1977). The crystals were finally filtered and air dried. Chanell (1971) and later Neels et al., (1978) have both shown that the buffering action of the complexing agent triethanolamine (TEA) in these silica gels slows down the nucleation rate, increases the SiO_2 content of the solution and leads to the formation of bigger crystals of NaX and NaA zeolites. Using this agent in the synthesis and diluting the gel with about 10 % TEA, larger crystals of makatite (IV) were formed.

The use of synthetic glasses instead of amorphous SiO_2 in the hydrothermal system has resulted in crystallization of a number of zeolite crystals (Fälth, 1980), where the choice of composition and particle size of the glass, pH and temperature have been shown to be very important. Some hydrothermal syntheses using sodialuminosilicate glass, NaOH and $\text{Ba}(\text{OH})_2$ solution and sodialuminosilicate glass, NaOH and CsCl solution yielded crystals of $\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2$ (I) and $\text{Cs}_{0.35}\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6$ (V).

Unit cell dimensions

Since the cell dimension for compound IV given by Sheppard et al. (1970) was questionable, small crystals were initially examined in a Philips EM400 electron microscope, to obtain preliminary crystallographic data. From the

diffraction pattern it was possible to calculate the unit cell axes. When sufficiently large crystals for single crystal X-ray work were obtained, space group and preliminary cell dimensions were determined, as for compounds I, II, III and V, using the Weissenberg technique. More accurate cell dimensions were obtained from least-squares refinement of $\sin^2\theta$ -values taken from powder photographs, using a Guinier-Hägg focusing camera. The radiation and internal standard used were $\text{CuK}\alpha_1$ ($\lambda = 1.54056 \text{ \AA}$) and KCl ($a = 6.2928 \text{ \AA}$), except for compound II where $\text{FeK}\alpha_1$ ($\lambda = 1.93604 \text{ \AA}$) and $\text{Pb}(\text{NO}_3)_2$ ($a = 7.8568 \text{ \AA}$) were used (Raade and Mladeck, 1983). The lines for I, IV and V were measured on a microfilm viewer (18x mag.) with visually estimated intensities. Crystal data for the investigated compounds are given in Table 1.

The reason for choosing the $\text{P2}_1/\text{n}$ and B2_1 unit cells for compounds II and V, instead of the standard $\text{P2}_1/\text{c}$ and P2_1 cells, is that the former cells correspond better with the morphology of the crystals. The unit cell parameters in space groups $\text{P2}_1/\text{c}$ and P2_1 are:

II $\text{P2}_1/\text{c}$ $a = 10.668$, $b = 9.787$, $c = 14.727 \text{ \AA}$, $\beta = 115.78^\circ$

III P2_1 $a = 7.3585$, $b = 5.0334$, $c = 8.737 \text{ \AA}$, $\beta = 114.12^\circ$

Data collection and reduction

The single crystal diffractometers used for collecting the data sets are:

A computer-controlled Enraf-Nonius CAD4 four-circle single crystal diffractometer

A Syntex Nicolet P3m

All calculations were carried out on the UNIVAC 1108 and VAX 11/780 computers at the University of Lund. The programmes used are described by Lundgren (1982).

The crystals used for data collection were selected with the Weissenberg technique. All intensity measurements were made with a single crystal diffractometer using ω - 2θ scan technique at room temperature. The radiation used was monochromatized by a graphite monochromator. A least-squares

Table 1. Crystal data

Compound		Space group	Z	Unit cell
I	$\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2$	$\overline{\text{P1}}$	2	$a = 7.0793(4)\text{\AA}$ $b = 7.3585(5)$ $c = 7.5814(5)$ $\alpha = 90.357(6)^\circ$ $\beta = 88.792(6)$ $\gamma = 91.793(6)$ $V = 394.7\text{\AA}^3$
II	Janhaugite $(\text{Na}, \text{Ca})_3(\text{Mn}, \text{Fe})_3(\text{Ti}, \text{Zr}, \text{Nb})_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{F}, \text{OH})_2$	$\text{P2}_1/\text{n}$	4	$a = 10.668(2)\text{\AA}$ $b = 9.787(4)$ $c = 13.931(3)$ $\beta = 107.82(2)^\circ$ $V = 1384.7\text{\AA}^3$
III	Kvanefjeldite $\text{Na}_4(\text{Ca}, \text{Mn})(\text{Si}_3\text{O}_7\text{OH})_2$	Pcab	4	$a = 10.213(4)\text{\AA}$ $b = 15.878(4)$ $c = 9.058(1)$ $V = 1465.0\text{\AA}^3$
IV	$\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$\text{P2}_1/\text{c}$	4	$a = 7.3881(5)\text{\AA}$ $b = 18.094(3)$ $c = 9.5234(5)$ $\beta = 90.64(1)^\circ$ $V = 1277.0\text{\AA}^3$
V	$\text{Cs}_{0.35}\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6$	B2_1	4	$a = 7.3585(4)\text{\AA}$ $b = 5.0334(3)$ $c = 15.950(1)$ $\beta = 90.778(9)^\circ$ $V = 590.7\text{\AA}^3$

refinement of a number of accurately determined θ -values was used to confirm the cell parameters. The stability of the instrument and the crystal was checked by measuring a few standard reflexions at regular intervals in each experiment.

All data sets were corrected for Lorentz, polarization and absorption effects. One independent set of reflexions was measured to as large a value of $\sin\theta/\lambda^0$ as reasonable, except for compound III where two sets of reflexions were measured. Information concerning the data collection and reduction are given in Table 2.

Determination and refinement of the structures

In compound I the Ba atoms were determined from the three-dimensional Patterson function and the other atoms from subsequent difference Fourier synthesis. All other structures were solved by direct methods (MULTAN) and difference Fourier calculations.

All the crystal structure refinements were made by full-matrix least-squares. The function minimized was $\sum w(|F_O| - |F_C|)^2$ with $w^{-1} = \sigma_C^2(|F_O|) + (c_1|F_O|)^2 + c_2$. The parameters c_1 and c_2 were adjusted to give constant value of $\langle w(\Delta F)^2 \rangle$ in different $|F_O|$ and $\sin\theta$ intervals. Further information on the structure refinements is given in Table 2.

Scattering factors for neutral atoms were used (Doyle and Turner, 1968, International Tables for X-ray Crystallography). Anomalous dispersion parameters were those of Cromer and Liberman (1970). Correction for isotropic secondary extinction (Zachariasen, 1968) was included in the final refinement.

In the structure of compound II and III, which have rather complex compositions, there is more than one metal atom type in the same oxygen polyhedron. The occupancy numbers for these atoms were calculated using the same positional parameters and temperature factors in the refinement.

In the final refinements anisotropic temperature factors were introduced for all non-H atoms except for Ca, Mn atoms in compound III. Refinement of the H coordinates and the isotropic temperature factor were successful in the kvanefjeldite structure (III), but in the $\text{Ba}_2[\text{SiO}_2(\text{OH})_2]$ structure (I)

Table 2. Data collection, reduction and refinement

Compound	I	II	III	IV	V
Apparatus	Nicolet P3m	Nicolet P3m	Nicolet P3m	CAD-4	Nicolet P3m
Crystal size (mm ³)	0.250x0.390x0.030	0.240x0.060x0.050	0.270x0.250x0.087	0.090x0.052x0.006	0.201x0.050x0.020
Radiation	MoK _α	MoK _α	CuK _α	CuK _α	CuK _α
θ-interval	1.5-40	3-40	2-57	5-70	1.5-57
μ (mm ⁻¹)	10.5	4.51	12.9	5.71	23.5
Range of transmission factors	0.24-0.72	0.78-0.86	0.10-0.45	0.73-0.97	0.32-0.52
Limit of I/σ _C (I)	3.0	3.0	3.0	2.0	3.0
No of reflexions:					
recorded	5193	5236	1887	2386	494
with zero weight	313	856	135	1552	14
in final refinement, m	4880	4380	1752	834	480
No of parameters refined, n	110	278	127	185	92
m/n	44.4	15.8	13.8	4.5	5.2
$R = \Sigma \Delta F / \Sigma F_o $	0.021	0.031	0.029	0.051	0.044
$R_w = [\Sigma w \Delta F ^2 / \Sigma w F_o ^2]^{1/2}$	0.028	0.034	0.041	0.055	0.054
$S = [\Sigma w \Delta F ^2 / (m-n)]^{1/2}$	0.70	1.09	0.81	1.52	1.01
g (x10 ⁻⁴) extinction	0.11	0.16	0.05	0.22	0.07

the approximation positions found in the Fourier map were used as fixed parameters with a given constant value of the isotropic temperature factors.

III DESCRIPTION OF THE STRUCTURES

This chapter gives a brief review of the structures of the compounds determined by the author. They represent silicate structures containing singular, primary, secondary, tertiary or quaternary SiO_4^{4-} -tetrahedra. Information on the silicate ions, the non-tetrahedral cations and molecules involved in the structures are given below.

Stereodrawings of the various structures of silicate ions are shown in Fig. 10-14.

Compound	Silicate ion	Type of SiO_4^{4-} -tetrahedra	Non-tetrahedral cation and molecules
I	$[\text{SiO}_2(\text{OH})_2]^{2-}$	singular	Ba^{2+}
II	$[\text{Si}_2\text{O}_7]^{6-}$	primary	Na^+ , Ca^{2+} , Mn^{2+} , Fe^{2+} , Ti^{4+} , Zr^{4+}
III	$[\text{Si}_3\text{O}_7(\text{OH})^{3-}]_n$	secondary, tertiary	Na^+ , Ca^{2+} , Mn^{2+}
IV	$[\text{Si}_2\text{O}_4(\text{OH})^{2-}]_n$	tertiary	Na^+ , H_2O
V	$[\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6^{0.35-}]_n$	quaternary	Cs^+

$\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2 \cdot (\text{I})$

The structure of compound I consists of discrete tetrahedra and Ba^{2+} -atoms (Fig. 10), the latter coordinated by nine tetrahedra oxygen atoms. The tetrahedra are connected by hydrogen bonds. Consequently, a pseudo framework is built up having the formula $[\text{SiO}_2(\text{OH})_2]_n^{2-}$.



Fig. 10. The structure of $\text{Ba}_2[\text{SiO}_2(\text{OH})_2]_2$ (I) projected along the z-axis

The result of an empirical bond strength calculation following Brown (1981) is shown in Table 3. The aim of this calculation was to check the position of the hydrogen bonds. As the positional parameters for the hydrogen atoms were taken from a Fourier map and not refined, the bond valence used in the calculation are taken from Brown (1976, Fig. 4). The valence sums are satisfactory with a maximum deviation of 4.8 % for O(5).

Table 3. Empirical bond strength calculation for compound I (valence unit)*

	Ba(1)	Ba(2)	Si(1)	Si(2)	H(11)**	H(26)***	H(36)	H(63)**	H(54)***	H(77)**	Σ
O(1)	0.183	0.277	0.979		0.50						1.939
O(2)	0.138	0.243	0.898			0.73					2.009
O(3)	0.132	0.266 0.090	0.932					0.50			1.920
O(4)	0.284	0.361	1.063						0.35		2.058
O(5)	0.197	0.176		0.882					0.65		1.905
O(6)	0.154	0.129		0.982		0.27		0.50			2.035
O(7)	0.220	0.228		0.966						0.50	1.914
O(8)	0.392 0.262	0.251		1.055							1.960
Σ	1.962	2.021	3.872	3.885	0.50	1.00		1.00	1.00	0.50	15.740

*Brown (1981)

**occupancy factor 0.5

***Brown (1976)

Janhaugite (II)

The structure of janhaugite (II) is built of columns of edge-sharing octahedra containing Mn, Ti(Zr) and Na(Ca) atoms in the c-direction. Four columns are linked into walls which are joined together as shown in Fig. 11. The $[\text{Si}_2\text{O}_7]^{6-}$ groups are placed in the space between the walls with the bridging oxygen (O(4) and O(11)) coordinated to Na(3). In this way the Na(3)O_6 -octahedra are replaced by Na(3)O_8 -polyhedra, which can be described as hexagonal bipyramids.

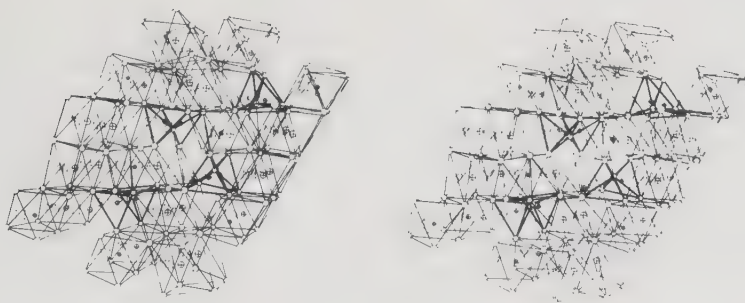


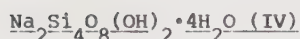
Fig. 11. The structure of janhaugite (II) projected along the c-axis. One half of the unit cell in the [001] direction is shown.

Kvanefjeldite (III)

The basis of the kvanefjeldite structure is a new type of silicate layer, $[\text{Si}_3\text{O}_7(\text{OH})]^{3-}$, containing only eight rings (Fig. 12). The layers are highly corrugated and are also examples of layers consisting of both secondary and tertiary tetrahedra. The layers are closely related to double layers containing rings of six tetrahedra, which are found in slices of the cristobalite structure. Na, Mn(Ca) and H atoms are placed between the layers, holding the layers together. Na atoms are also situated within the layers. The hydrogen positional parameters are refined. The angle O(7)-H-O(3) is 176.2° and the O(7)-H distance is 0.78 Å. The short O(7)-H distance depends on the X-ray method which measures the position of electron density maxima, rather than the position of the atomic nuclei.



Fig. 12. The $[\text{Si}_3\text{O}_7(\text{OH})^{3-}]_n$ layer found in kvanefjeldite (III) projected along $[010]$



The structure of compound IV is built up of single layers containing rings of six SiO_4^{4-} tetrahedra (Fig. 13) similar to those found in sanbornite, ($\text{Ba}_2\text{Si}_4\text{O}_{10}$; Douglass, 1958). The layers are held together by Na atoms, and the silicate layers and Na atoms in this way form a framework containing channels, parallel to the a-axis, in which columns of edge-sharing $[\text{Na}(\text{H}_2\text{O})_4]_n^{n+}$ octahedra are placed.



Fig. 13. A stereoview of a single layer in makatite (IV) projected along $[010]$

The hydrogen atoms were not located in the structure refinement. From an empirical bond strength calculation (Brown, 1981) and interatomic oxygen-oxygen distances it is possible to find oxygen atoms which are bonded to hydrogen atoms (O-H) or involved in hydrogen bonding (O---H). The valence sum for these oxygen atoms should be lower than 2 v.u. From the results in Table 4 it is obvious that proper atoms are O(7)-O(10) and W(1)-W(4). A number of interatomic oxygen-oxygen distances ($<3 \text{ \AA}$), including these oxygen atoms, is listed on the next page.

Table 4. Exmpirical bond strength calculation for compound IV (valence unit)*

	Na(1)**	Na(2)**	Na(3)	Si(1)	Si(2)	Si(3)	Si(4)	Σ
O(1)				1.041			1.019	2.060
O(2)				0.964			1.030	1.994
O(3)				1.052	1.027			2.079
O(4)					0.992	0.997		1.989
O(5)					0.997	0.964		1.961
O(6)						1.011	1.019	2.030
O(7)				1.075				1.075
O(8)			0.148		1.030			1.178
O(9)			0.187			1.122		1.309
O(10)			0.206				1.069	1.275
W(1)	0.169	0.170						0.339
W(2)	0.151	0.166						0.317
W(3)		0.141	0.212					0.353
W(4)	0.186		0.194					0.380
Σ	0.506	0.477	0.947	4.132	4.046	4.094	4.137	18.339

*Brown (1981)

**placed at symmetry centre

O(7)-O(8)	2.499 Å
O(9)-O(10)	2.582 Å
W(1)-O(5)	2.990 Å
W(1)-O(8)	2.795 Å
W(2)-O(2)	2.985 Å
W(2)-O(7)	2.766 Å
W(3)-O(7)	2.714 Å
W(4)-O(9)	2.719 Å

The suggested bond strength calculation, including the hydrogen atoms shown in Table 5, is based on the following observations.

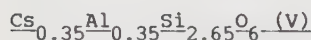
The very low valence sums for W(1), W(2), W(3) and W(4) (~ 0.3 v.u.) indicate that eight hydrogen atoms are bonding to the oxygen atoms in H_2O molecules. The two remaining hydrogen atoms are placed between O(7)-O(8) and O(9)-O(10) because of the low valence sums and the short oxygen-oxygen distances. The possible hydrogen bond from W(1) and W(2) is, except for the oxygen-oxygen distances, based on the angles O(5)-W(1)-O(8) and O(2)-W(2)-O(7) which are 112.1° and 113.6° respectively.

The valence used in the calculation is based on hydrogen bond oxygen-oxygen distances (Brown, 1976, Fig. 4).

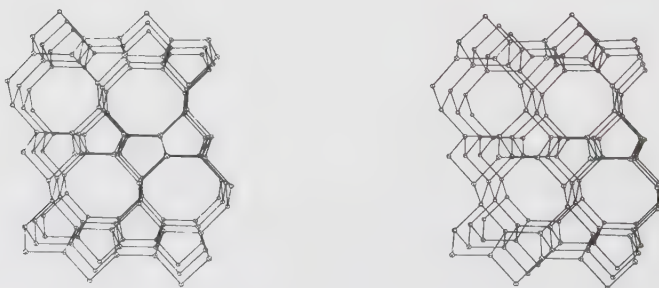
Table 5. Suggested balance for compound IV (valence unit)*

	Σ	H(78)	H(910)	H(15)	H(18)	H(22)	H(27)	H(37)	H(3)	H(49)	H(4)	Σ
O(1)	2.060											2.06
O(2)	1.994					0.11						2.10
O(3)	2.079											2.08
O(4)	1.989											1.99
O(5)	1.961			0.11								2.07
O(6)	2.030											2.03
O(7)	1.075	0.41					0.20	0.23				1.92
O(8)	1.178	0.59			0.18							1.95
O(9)	1.309		0.32							0.23		1.86
O(10)	1.275		0.68									1.96
W(1)	0.339			0.89	0.82							2.05
W(2)	0.317					0.89	0.80					2.01
W(3)	0.353							0.77	1.0			2.12
W(4)	0.380									0.77	1.0	2.15
Σ	18.339	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	28.34

*Brown (1976)



The structure consists of an aluminosilicate framework isotypical with that found in bikitaite (Kocman et al., 1974). Connected eight and five tetrahedral rings form the framework (Fig. 14). The Cs atoms are placed close to the centre of the channels built up of the eight rings in the [010] direction. The occupancy factor of Cs was refined to 0.35. The aluminium content in the tetrahedra seems to be statistically distributed, about 12 % Al in each tetrahedron. The mean interatomic (Si,Al)-O distances for each tetrahedron are approximately the same (~1.61 Å).

Fig. 14. The framework of $\text{Cs}_{0.35}\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6$ projected along [010]

IV THE VARIATION OF Si-O BOND LENGTHS

Compounds I-V are built up of different silicate ions and different non-tetrahedral cations. The number of unshared oxygen atoms in the SiO_4^{4-} tetrahedra varies. A study of the Si-Si and Si-O distances in the structures shows that these are in the ranges 2.95-3.16 Å and 1.57-1.67 Å respectively. This variation in the distances seems to be normal in silicates which can be seen in a histogram of Si-Si and Si-O distances given by O'Keefe and Hyde (1978, Fig. 1) and Hill and Gibbs (1979, Fig. 3).

During the last twenty years there have been several studies devoted to an understanding of the variation in the Si-O distances. A number of parameters have been investigated to see whether there is any correlation between these and the Si-O distances. Various theories to explain the correlations have been presented. Some factors which have been investigated are:

1. Sum of bond strengths
2. Mean coordination of the oxygen atoms
3. Influence of the non-tetrahedral cations
4. The Si-O-Si angles
5. The O-Si-O angles

The possible relationships between these factors and the Si-O distances in compounds I-V will be discussed in the next paragraphs.

Table 6 presents some data concerning the Si-O distances in compounds I-V.

Table 6. Si-O distances

Compound	Number of Si-O distances	d(Si-O)/Å range	d(Si-O)/Å mean	$\sigma^*/\text{Å}$
I	8	1.599-1.670	1.635	0.002
II	16	1.592-1.645	1.622	0.002
III	12	1.570-1.649	1.621	0.002
IV	16	1.579-1.636	1.613	0.009
V	12	1.594-1.637	1.612	0.011

*max e.s.d. in d(Si-O)

Sum of bond strengths

Pauling (1929) defined for complex ionic compounds an electrostatic bond strength on an anion due to a cation as

$$s = \frac{z}{\text{C.N.}}$$

where z is the formal charge of the cation and C.N. is the coordination number of the cation. With this definition, he then proposed that if the anion is coordinated to other cations the sum of the electrostatic bond strengths, P (anion), will be exactly or nearly equal to the valence of the anion with changed sign.

Since Pauling made this postulate a great number of crystal structures have been determined. However, in many of these structures large deviations from this postulate are evident. The first to relate this deviation to variations in the Si-O distances was Smith (1953). He found that lower values on $P(O)$ correspond to shorter Si-O distances and vice versa.

The relationship between Si-O distances and $P(O)$ has been investigated by Baur (1970). In 293 Si-O distances he found a positive correlation between bond strength sums and Si-O distances and a linear regression of $d(\text{Si-O})$ on $P(O)$ gave the following equation:

$$d(\text{Si-O}) = 1.440 + 0.091 \cdot P(O)$$

Prediction of Si-O distances using bond strength sums has also been studied by Baur (1971, 1981, 1982).

According to Baur, the explanation to this relationship is, "that we are observing the induced effects of the 'other' cations on the Si-O covalent bonds". Thus, this relationship does not exist for SiO_2 modifications, because in these compounds there are no 'other' cations. The $P(O)$ values are equal to 2 v.u. for all oxygen atoms. Some effects of the 'other' cations will be discussed in the next two paragraphs.

The validity of this relationship for compounds I-V, is displayed in a plot of $d(\text{Si-O})$ versus $P(O)$ (Fig. 15). Bond strength calculations for the compounds are given in Tables 8-12. The variation of $P(O)$ and the Si-O distances are summarized on the next page.

	range P(O)/v.u.	range d(Si-O)/Å	Symbols in Fig. 15
I	1.61-2.27	1.599-1.670	■
II	1.69-2.33	1.592-1.645	△
III	1.70-2.20	1.570-1.649	▲
IV	1.70-2.17	1.579-1.636	●
V	1.94-2.05	1.594-1.637	○

Notwithstanding the paucity of points for each compound, it is interesting to calculate regression equations for each compound and compare the results with those of Baur (1970). The results of a regression analysis of d(Si-O) on P(O) are given in Table 7, where a and b are constants in the equation $d(\text{Si-O}) = a + b \cdot P(\text{O})$, N = number of points in sample and r = correlation coefficient.

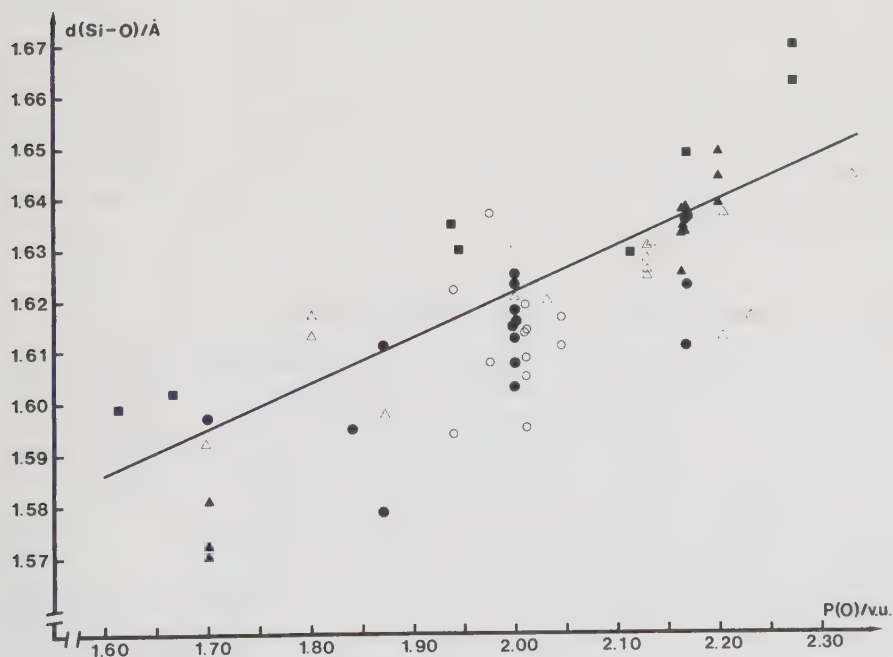


Fig. 15. Plot of d(Si-O) versus P(O). The solid line corresponds to the regression line, $d(\text{Si-O}) = 1.440 + 0.091 \cdot P(\text{O})$ (Baur, 1970).

Of course, the bond strength sum calculation for compound IV is uncertain, because the positions of the hydrogen atoms are based on conjecture. The solid line in Fig. 15 corresponds to the regression equation found by Baur

Table 7. Results of regression analysis

Compound	a	b	N	r
I	1.442	0.096	8	0.96
II	1.507	0.056	16	0.75
III	1.351	0.131	12	0.98
IV	1.450	0.081	16	0.73
V	1.597	0.007	12	0.02
I-IV	1.436	0.091	52	0.81
Baur (1970)	1.440	0.091	293	0.69

(1970), $d(\text{Si-O}) = 1.440 + 0.091 \cdot P(\text{O})$. It is obvious that this relationship holds for compounds I-IV but not for V, which depends on the small variation in $P(\text{O})$, 1.940-2.047 v.u. The Cs atoms in the structure seems to have no influence on the Si-O distances. The regression equation for the observed data in compounds I-IV is in good agreement with that found by Baur (see Table 7). The points are scattered around the line. From Table 6 it can be seen that the points below the line are in general from compounds with the lowest mean values, and vice versa.

Table 8. Bond strength calculation for compound I (valence unit)

	Ba(1)	Ba(2)	Si(1)	Si(2)	H(11)*	H(26)	H(36)	H(63)*	H(54)	H(77)*	Σ
O(1)	0.22	0.22	1.00		0.50						1.94
O(2)	0.22	0.22	1.00			0.83					2.27
O(3)	0.22	0.44	1.00					0.50			2.16
O(4)	0.22	0.22	1.00						0.17		1.61
O(5)	0.22	0.22		1.00					0.83		2.27
O(6)	0.22	0.22		1.00		0.17		0.50			2.11
O(7)	0.22	0.22		1.00						0.50	1.94
O(8)	0.44	0.22		1.00							1.66
Σ	1.98	1.98	4.00	4.00	0.50	1.00		1.00	1.00	0.50	15.96

*occupancy factor 0.5

Table 9. Bond strength calculation for compound II (valence unit)

	Mn(1)	Mn(2)	Mn(3)	Ti(1)	Ti(2)	Na(1)	Ca(1)	Na(2)	Ca(2)	Na(3)	Ca(3)	Si(1)	Si(2)	Si(3)	Si(4)	Σ
O(1)	0.33							0.23		0.13		1.00				1.69
O(2)					0.67					0.13		1.00				1.80
O(3)		0.33	0.33		0.67							1.00				2.33
O(4)										0.13		1.00	1.00			2.13
O(5)		0.33			0.67			0.23					1.00			2.23
O(6)				0.67						0.13			1.00			1.80
O(7)			0.33	0.67		0.21							1.00			2.21
O(8)		0.33	0.33			0.21								1.00		1.87
O(9)			0.33	0.67										1.00		2.00
O(10)	0.33			0.67						0.13				1.00		2.13
O(11)										0.13				1.00	1.00	2.13
O(12)	0.33			0.67		0.21									1.00	2.21
O(13)			0.33		0.67										1.00	2.00
O(14)					0.67			0.23		0.13					1.00	2.03
O(15)	0.33	0.33			0.67			0.23								1.56
O(16)	0.33	0.33		0.67		0.21										1.54
F(1)		0.33				0.41				0.13						0.87
F(2)	0.33		0.33					0.46								1.12
Σ	1.98	1.98	1.98	4.02	4.02	1.25		1.38		1.04		4.00	4.00	4.00	4.00	33.65

Table 10. Bond strength calculation for compound III (valence unit)

	Ca(Mn)*	Na(1)	Na(2)	Si(1)	Si(2)	Si(3)	H	Σ
O(1)			0.17	1.00	1.00			2.17
O(2)	0.33	0.20	0.17	1.00				1.70
O(3)	0.33	0.20				1.00	0.17	1.70
O(4)	0.33	0.20	0.17		1.00			1.70
O(5)			0.17	1.00		1.00		2.17
O(6)			0.17	1.00		1.00		2.17
O(7)		0.20	0.17		1.00		0.83	2.20
O(8)		0.20			1.00	1.00		2.20
Σ	0.99	1.00	1.02	4.00	4.00	4.00	1.00	16.01

*placed at a symmetry centre

Table 11. Bond strength calculation for compound IV (valence unit)

Na(1)*	Na(2)*	Na(3)	Si(1)	Si(2)	Si(3)	Si(4)	H(78)	H(910)	H(15)	H(18)	H(22)	H(27)	H(37)	H(3)	H(49)	H(4)	Σ
O(1)			1.00			1.00											2.00
O(2)			1.00			1.00					0.17						2.17
O(3)			1.00	1.00													2.00
O(4)			1.00	1.00	1.00												2.00
O(5)			1.00	1.00	1.00				0.17								2.17
O(6)			1.00	1.00	1.00	1.00											2.00
O(7)			1.00				0.5					0.17	0.17				1.84
O(8)		0.20		1.00			0.5			0.17							1.87
O(9)		0.20			1.00			0.5							0.17		1.87
O(10)		0.20				1.00											1.70
W(1)	0.17	0.17															2.00
W(2)	0.17	0.17															2.00
W(3)	0.17																2.00
W(4)	0.17	0.20															2.20
Σ	0.51	0.51	1.00	4.00	4.00	4.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	28.02

*placed at a symmetry centre

Table 12. Bond strength calculation for compound V (valence unit)

	Cs*	Si(1)**	Si(2)**	Si(3)**	Σ
O(1)	0.07	1.94			2.01
O(2)	0.04		1.94		1.98
O(3)				1.94	1.94
O(4)	0.07	0.97	0.97		2.01
O(5)	0.07	0.97		0.97	2.01
O(6)	0.11		0.97	0.97	2.05
Σ	0.36	3.88	3.88	3.88	12.00

*occupancy factor 0.35

**calculated for $\text{Si}_{0.88}\text{Al}_{0.12}$

Mean coordination of the oxygen atoms

The mean Si-O distance, $\overline{d(\text{Si-O})}$, varies between 1.612 Å (in V) to 1.635 Å (in I). In 1963 Smith and Baily observed that $\overline{d(\text{Si-O})}$ varies from 1.61 Å in tectosilicate to 1.63 Å in orthosilicate. They pointed out that there was a relationship between $\overline{d(\text{Si-O})}$ and the degree of condensation of the SiO_4^{4-} tetrahedra.

The correspondences between Si-O distances and the coordination of the oxygen atoms were later observed by, among others, Gibbs (1966) and Gibbs et al. (1968). They found that the Si-O distances were on average shorter when the coordination numbers for the oxygen atoms were low.

In 1969 Brown and Gibbs found that the mean Si-O distance in any structure varies with the mean coordination number of the oxygen atoms ($\overline{\text{C.N. O}}$). This correlation can be explained in different ways. One explanation is the hybridization of the atomic orbitals of oxygen, where oxygen atoms with larger coordination numbers lead to less s-character in the bond. Another explanation, given by Shannon and Prewitt (1969), is the change of anion radius with the coordination number. The radius for O^{2-} increase from 1.35 Å (C.N. = 2) to 1.38 Å (C.N. = 4).

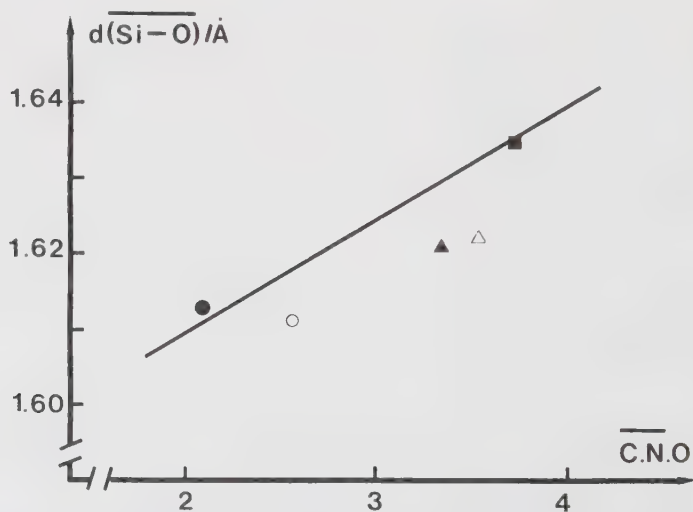
The oxygen atoms in the silicate ions coordinate to silicon atoms and non-tetrahedral cation (M). When the variations of M-O distances in a MO-polyhedron are small, there are often clear cut-off points for which we may consider peripheral anions as being bonded to M. In this case it is easy to determine the coordination. However, when M is an alkali- or alkali earth-ion there is often a gradual increase in the M-O distances, and the coordination numbers for these ions are uncertain. An example of this is the Na(3)-O distances in II, where the distance increases gradually from 2.296 Å to 2.867 Å. Some data concerning the M-O polyhedra and $\overline{\text{C.N. O}}$ for I-V are given in Table 13. A break of 0.2 Å has been used as the cut-off point in the M-O distances.

A plot is given of $\overline{d(\text{Si-O})}$ versus $\overline{\text{C.N. O}}$ in Fig. 16. ($\overline{d(\text{Si-O})}$ values are given in Table 6). The solid line corresponds to the regression equation found by Brown and Gibbs (1969): $\overline{d(\text{Si-O})} = 0.015 \overline{\text{C.N. O}} + 1.579$. With only five points in the diagram it is difficult to draw any conclusions, but there is a trend of increasing $\overline{d(\text{Si-O})}$ with increasing $\overline{\text{C.N. O}}$. The short

Table 13. Bond lengths and coordination numbers

Compound	$\overline{\text{C.N. O}}$	M	$d(\text{M-O})/\text{\AA}$ range	C.N. M	MO-polyhedra
I	3.75	Ba	2.626-3.24	9	capped square anti-prism
II	3.57	Ti	1.830-2.268	6	octahedra
		Mn	2.068-2.313	6	octahedra
		Na(1,2)	2.236-2.539	6	octahedra
		Na(3)	2.218-2.867	8	hexagonal bipyramid
III	3.38	Ca	2.292-2.379	6	octahedra
		Na(1)	2.292-2.487	5	trigonal bipyramid
		Na(2)	2.296-2.681	6	trigonal prism
IV	2.10- 2.30*	Na(3)	2.328-2.532	5	trigonal bipyramid
V	2.58	Cs	3.246-3.578	10	irregular

*depend on the position of the hydrogen atoms

Fig. 16. Plot of $d(\text{Si-O})$ versus $\overline{\text{C.N. O}}$. The solid line from Brown and Gibbs (1969). ■ (I); △ (II); ▲ (III); ● (IV); ○ (V).

mean Si-O distances for III is probably an effect of the low electronegativity values for the sodium and calcium atoms, resulting in shortening of the Si-O distances (see next paragraph).

Influence of the non-tetrahedral cations

The oxygen atoms in a silicate ion which are bonded to two silicon atoms are called bridging oxygen atoms, Obr, and those which are bonded to one silicon atom alone are called non-bridging oxygen atoms, Onbr. The difference in the distances between $d(\text{Si-Obr})$ and $d(\text{Si-Onbr})$ depends on the electronegativity of the non-tetrahedral cation which is bonded to Onbr (Noll, 1963). Shorter $d(\text{Si-Onbr})$ distances are associated with less electronegative non-tetrahedral cations. The influence of the electronegativity of the cations on the Si-Onbr distances has been discussed by, among others, MacDonald and Cruickshank (1967), Brown and Gibbs (1969, 1970), Jones and Taylor (1968) and Pant and Cruickshank (1967).

As mentioned earlier, the SiO_4^{4-} -tetrahedra are called singular, primary etc. depending on number of unshared oxygen atoms. These tetrahedra are in Table 14 denoted T_0 , T_1 , T_2 , T_3 and T_4 . The mean Si-O distances, given in Table 14 for different types of tetrahedra, are divided into three groups based on the coordination of the oxygen atoms. The three groups are:

1. oxygen atoms bonded to two silicon atoms, $d(\overline{\text{Si-OSi}})$,
2. oxygen atoms bonded to one silicon atom and one hydrogen atom, $d(\overline{\text{Si-OH}})$,
3. oxygen atoms bonded to one silicon atom and one non-tetrahedral atom M, where $\chi_M < \chi_{\text{Si}}$ (χ = electronegativity), $d(\overline{\text{Si-OM}})$.

The values of $d(\overline{\text{Si-O}})$ in different types of SiO_4^{4-} -tetrahedra (T_n) is shown in Fig. 17. In Table 14 two Si-O distances are given for compound I in group 2, 1.667 Å and 1.636 Å. The latter value is for $d(\overline{\text{Si-Onbr}})$, where Onbr are bonded to partially occupied hydrogen atoms. This could explain why this mean distance is shorter than the former value. The distance of 1.596 Å given for compound IV is placed between group 2 and 3 because the position of the hydrogen atoms are not known. The short Si-Onbr distances (Onbr = O(7)-O(10)) indicate that the hydrogen atoms are placed between O(7)-O(8) and O(9)-O(10) (cf. le Bihan et al., 1971).

Table 14. Mean Si-O distances

Compound	Group 1 $\overline{d(\text{Si}-\text{OSi})}/\text{\AA}$	Group 2 $\overline{d(\text{Si}-\text{OH})}/\text{\AA}$	Group 3 $\overline{d(\text{Si}-\text{OM})}/\text{\AA}$	T_n
I		1.667 1.636	1.601	T_0
II	1.628		1.619	T_1
III	1.641 1.634	1.649	1.572 1.576	T_2 T_3
IV	1.619	$\leftarrow 1.596 \rightarrow$		T_3
V	1.612			T_4

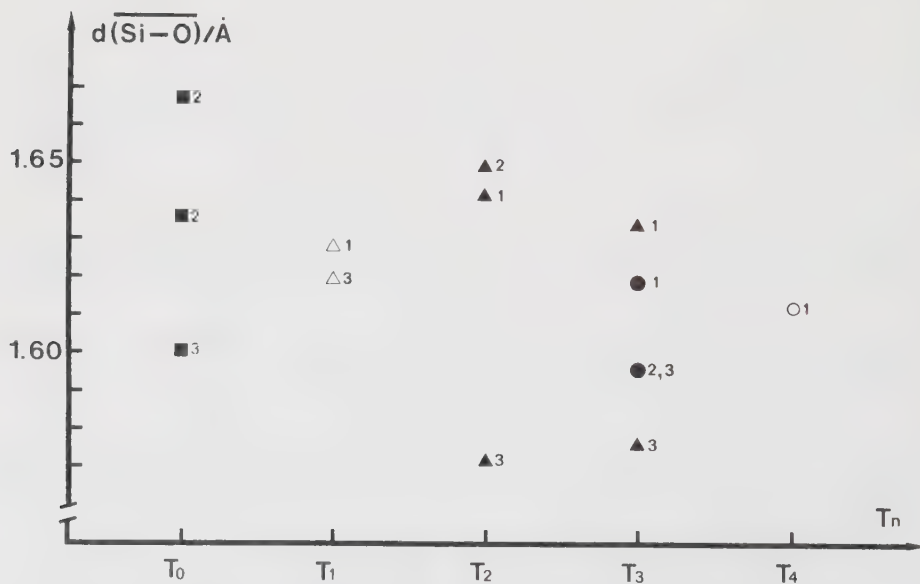


Fig. 17. $\overline{D(\text{Si}-\text{O})}$ in different types of SiO_4^{4-} -tetrahedra (T_n). ■ (I); △ (II); ▲ (III); ● (IV); ○ (V).

In compounds I and III there are clear differences in the Si-Onbr distances when Onbr are bonded to hydrogen atoms ($\chi_{\text{H}} > \chi_{\text{Si}}$) or M ($\chi_{\text{M}} < \chi_{\text{Si}}$). To find

a correlation between the Si-O distances and the electronegativity of the cations in the structures is of no use, since the structures are quite different. However, in general it is evident that in each compound $d(\text{Si-OH}) > d(\text{Si-OSi}) > d(\text{Si-OM})$, although the differences are small in some cases.

The Si-O-Si angles

Even when the sum of the covalent radii in a Si-O bond has been corrected for partial ionic character, the observed distance is shorter than that calculated (Schomaker and Stevenson, 1941). Pauling (1952) explained this bond distance shortening by the existence of d-p π -bonding. Cruickshank (1961) showed that two strong π -bonding molecular orbitals may be formed between two 2p-orbitals of the oxygen atom and two of the five 3d-orbitals of the silicon atom. This means that there should be a relationship between the Si-Obr distances and the Si-O-Si angles. Since maximum d-p orbital overlap is obtained at 180° , this should lead to the shortest Si-Obr distances.

This relationships between the Si-Obr distances and the Si-O-Si angles can also be explained in terms of the classic valence bond theory and the valence-shell electron-pair repulsion theory, VSEPR (Gillispie, 1963). In the classic valence bond theory the oxygen atoms have varying hybridization states. The bonding orbitals are assumed to vary continuously between sp^2 and sp. The Si-Obr distances decrease as the s-content in the bonding orbital increases. In the second theory, VSEPR, the repulsion between two bonding electron pairs or between bonding electron pairs and non-bonding electron pairs influence the Si-O-Si angles. An increase of the percentage of π -bond character in the Si-Obr bonds leads to an increase of bond repulsion and the Si-O-Si angles become wider.

Correlation between the Si-Obr distances and the Si-O-Si angle has been the subject of much discussion. There have been a number of studies where the results have been ambiguous. Investigation of the framework silicates (Brown et al., 1969) indicates a relationship between distances and angles, where ~50 % of the variation in Si-Obr distances can be explained in terms of a linear dependence on the Si-O-Si angles. The dependence was greater for the silica polymorphs than for other silicates. Similar results are obtained for a number of silicates containing both Obr and Onbr. A better linear dependence is obtained if $d(\text{Si-Obr})$ is plotted against either the

hybridization index, λ ($= -1/\cos\langle\text{SiOSi}\rangle$ defined by the superscript sp^λ), or the fraction s-character, $f_s(\text{O}) = (1 + \lambda)^{-1}$ of the bridging oxygen atoms (cf. Brown and Gibbs, 1970; Gibbs, 1982; Gibbs et al., 1972, 1981, and Hill and Gibbs, 1979).

Baur (1971) showed that there exists a correlation between the Si-Obr distances and the Si-O-Si angles in a number of $\text{Si}_2\text{O}_7^{6-}$ -groups, but he concluded that the correlation follows from the influence of the non-tetrahedral cations. It is possible for Obr to coordinate non-tetrahedral cations, $P(\text{Obr}) > 2$, at narrow Si-O-Si angles. When Obr is 'overbonded' the Si-Obr distance will be longer than the mean Si-Obr distance in a SiO_4^{4-} -tetrahedron. Later Baur (1971, 1977) found a very low correlation in some SiO_2 -modifications.

O'Keeffe and Hyde (1978) have observed correlations between $d(\text{Si-Obr})$ and Si-Obr-Si angle for angles smaller than 145° .

The Si-O-Si angles can vary in a broad range from $\sim 125^\circ$ to 180° . A histogram of Si-O-Si angles is given by Tossell and Gibbs (1978, Fig. 5), where the mean angle is 144° .

Table 15 shows the two individual Si-Obr distances to a bridging oxygen atom, the difference between the distances ($\Delta d(\text{Si-Obr})$), the Si-Obr-Si angles (θ) and the hybridization index λ . In order to learn whether there is a relationship between the distances and λ , a plot of $d(\text{Si-Obr})$ vs. λ was prepared, see Fig. 18. The solid line in the diagram corresponds to the regression equation $d(\text{Si-Obr}) = 0.080 \cdot \lambda + 1.530$ (Hill and Gibbs, 1979).

As in Fig. 15, the points below the line are mostly from compounds with the lowest mean Si-O distances (IV and V). Compounds II and III, which have the lowest Δ -values and e.s.d. in the bond distances agree very well with the result found by Hill and Gibbs. The points are scattered in compounds IV and V where the e.s.d.'s in the bond distances are ~ 0.010 Å and the Δ -values vary. Largest Δ -values, ~ 0.03 Å, are between the symmetry-related distances (Si(2)-O(2), Si(2)-O(2ⁱⁱⁱ); Si(3)-O(3ⁱⁱⁱ), Si(3)-O(3)) in compound V. Using the mean Si-O distances around the bridging oxygen atoms, the relationship seems to hold for this compound. The short Si-O distances at narrow Si-O-Si angles (Si(1)-O(1)-Si(4), Si(2)-O(4)-Si(3)) found in compound IV are not consistent with this relation.

Table 15. Si-O distances and Si-O-Si angles

Compound	Si-Obr-Si	d(Si-Obr)/Å	d(Obr-Si)/Å	Δd(Si-Obr)/Å	θ/°	λ
II	Si(1)-O(4)-Si(2)	1.626(2)	1.625(2)	0.001	153.3(2)	1.119
	Si(3)-O(11)-Si(4)	1.631(2)	1.631(2)	0.000	149.7(2)	1.158
III	Si(1)-O(1)-Si(2)	1.625(2)	1.638(2)	0.013	144.5(1)	1.228
	Si(1)-O(5)-Si(3)	1.633(2)	1.634(2)	0.001	139.8(1)	1.309
	Si(1)-O(6)-Si(3)	1.638(2)	1.633(2)	0.005	143.8(1)	1.239
	Si(2)-O(8)-Si(3)	1.644(2)	1.639(2)	0.005	134.4(1)	1.429
IV	Si(1)-O(3)-Si(2)	1.603(8)	1.612(8)	0.009	147.9(6)	1.180
	Si(1)-O(2)-Si(4)	1.636(8)	1.611(8)	0.025	138.3(5)	1.339
	Si(1)-O(1)-Si(4)	1.607(9)	1.615(9)	0.008	132.2(6)	1.489
	Si(2)-O(5)-Si(3)	1.623(8)	1.636(8)	0.013	137.6(5)	1.354
	Si(2)-O(4)-Si(3)	1.625(9)	1.623(9)	0.002	132.4(6)	1.483
	Si(3)-O(6)-Si(4)	1.618(8)	1.615(8)	0.003	150.1(6)	1.153
V	Si(1)-O(1)-Si(1)	1.605(10)	1.614(10)	0.009	151.2(5)	1.141
	Si(1)-O(4)-Si(2)	1.614(8)	1.595(8)	0.019	154.6(6)	1.107
	Si(1)-O(5)-Si(3)	1.609(8)	1.619(8)	0.010	145.6(6)	1.212
	Si(2)-O(2)-Si(2)	1.608(9)	1.637(10)	0.029	145.1(6)	1.219
	Si(2)-O(6)-Si(3)	1.611(8)	1.617(7)	0.006	146.6(5)	1.198
	Si(3)-O(3)-Si(3)	1.622(11)	1.594(9)	0.028	148.4(6)	1.174

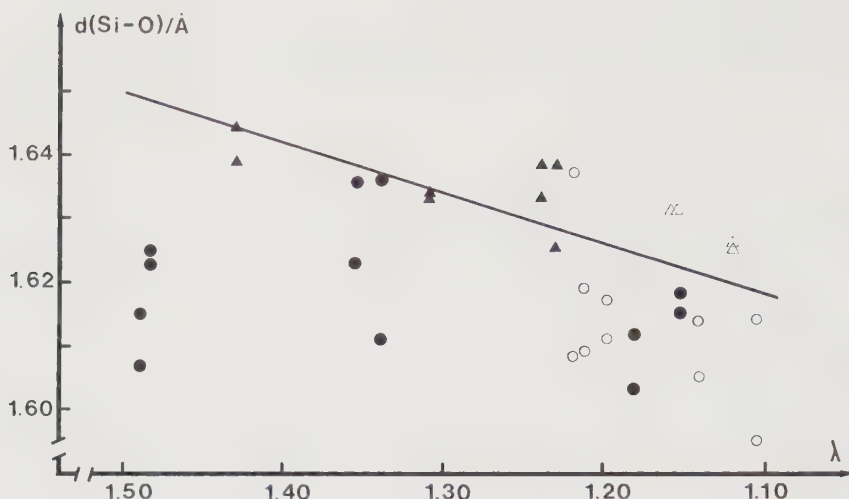


Fig. 18. Variation of $d(\text{Si-O})$ with λ . Δ (II); $\blacktriangle$ (III); $\bullet$ (IV); $\circ$ (V). The solid line corresponds to the regression equation $d(\text{Si-Obr}) = 0.080 \cdot \lambda + 1.530$ (Hill et al., 1979).

The O-Si-O angles

As mentioned earlier, there is a difference in the Si-O distances where the silicon atoms are bonded to bridging oxygen atoms or non-bridging oxygen atoms. In a SiO_4^{4-} -tetrahedron the bonds will repel another (Gillispie, 1963) in such a way that the O-Si-O angles should decrease in the order $\text{Onbr-Si-Onbr} > \text{Obr-Si-Onbr} > \text{Obr-Si-Obr}$. This theory holds for compound II where the Onbr-Si-Onbr angle range is $108.4\text{--}117.3^\circ$ and the Onbr-Si-Obr angle is $102.1\text{--}108.9^\circ$. In compound III the Onbr-Si-Obr angle range is $106.7\text{--}117.2^\circ$ and the Obr-Si-Obr angle range is $101.3\text{--}108.7^\circ$ which is also consistent with the theory, but the Onbr-Si-Onbr angle found in the Si(2)-tetrahedron (O(4)-Si(2)-O(7)) is only 110.4° . This low value of the angle is a result of the hydrogen atom bonded to O(7).

Using the mean value of the three angles formed with the bridging Si-O bond, $(\text{O-Si-O})_3$, it has been shown that there is a relationship between the variation of the Si-O distances and $(\text{O-Si-O})_3$ (Louisnathan and Gibbs, 1972, Louisnathan et al., 1977).

Recently a multiple linear regression analysis was calculated for a number of framework silicates where the variation in the Si-O distances could be explained in terms of a linear dependence on $P(O)$, $f_s(O)$ and $f_s(Si)$ (Geisinger et al., 1985). $f_s(Si)$ is defined in the same way as $f_s(O)$ such that $f_s(Si) = 1/1 - \sec\langle OSiO \rangle_3$ and measures the hybridization state of the silicon atoms. The parameters used in the calculation are associated with different bonding models.

The relationship between the Si-O distances and $f_s(Si)$ for compounds I-V is shown in a plot of $d(Si-O)$ versus $f_s(Si)$ (Fig. 19). The plot indicates a correlation. The points are as usual scattered, but shorter Si-O distances are associated with wider angles or larger $f_s(Si)$ values and vice versa.

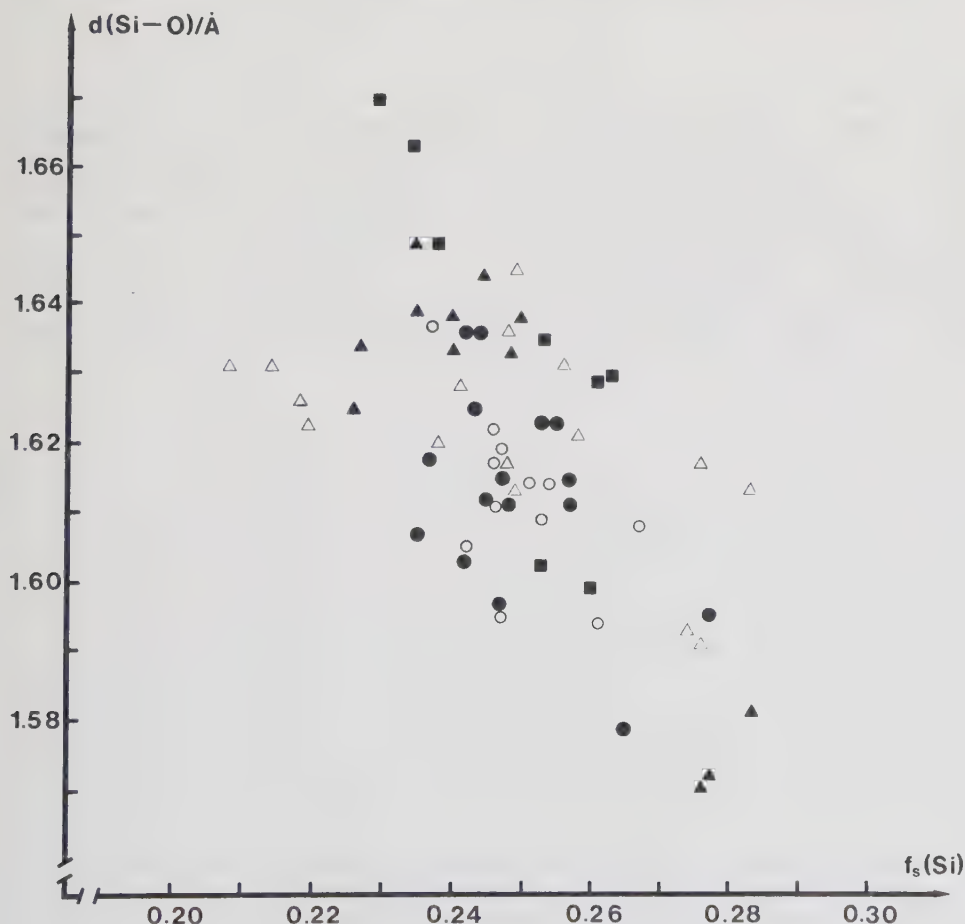


Fig. 19. Plot of Si-O distances versus $f_s(Si)$. ■ (I); △ (II); ▲ (III); ● (IV); ○ (V).

V SUMMARY

The Si-O distance variations can be partially explained in terms of bond strength sums at the oxygen atoms, the mean coordination at the oxygen atoms, the influence of the non-tetrahedral cations, the Si-O-Si angles and the O-Si-O angles. The problem is the small variation in the Si-O distances. In order to establish relationships unequivocally it is necessary to have accurate data. Each relationship discussed above seems to have its drawbacks. In SiO_2 -modifications and compounds, with bond strength sums at the oxygen atoms equal or almost equal to 2.0, there are no relationships with the bond distances. It is a problem to determine the mean coordination number at the oxygen atoms when the M-O distances increase gradually, and the difference in the Si-Obr distances around a bridging oxygen atom could be large.

The dependence of Si-O bond lengths on various parameters in the investigated compounds agree in general with those found in other silicates. The mean Si-O bond length varies from about 1.61 Å in V (tektosilicate) to about 1.64 Å in I (nesosilicate). The Si-Onbr distances are shorter than the Si-Obr distances except where Onbr is bonded to hydrogen atoms. The Si-Obr bonds become shorter as the angle at Obr increases. Studying the SiO_4^{4-} -tetrahedra reveals a connection with the Si-O distances and the angle around the silicon atom.

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